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Spatial and temporal variations in selected heavy metals in water and sediment from the Mhlathuze Estuary, Richards Bay

H. M. Mzimela^{1*}, V. Wepener² and D. P. Cyrus¹

¹University of Zululand, Private Bag X1001, KwaDlangezwa 3886, South Africa.

²Department of Zoology, University of Johannesburg, P.O. Box 523, Auckland Park 2006, South Africa.

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Spatial and temporal variations in water (total, dissolved and particulate), and sediment concentrations of seven heavy metals, Al, Cr, Cu, Mn, Pb and Zn from the Mhlathuze Estuary were analyzed. Effects of environmental factors on the metals in the estuary were also investigated. In water, metals concentrations varied spatially as well as seasonally with highest concentrations of Al, Cr, Fe, Mn and Zn recorded in summer. Partitioning of metals was influenced by environmental factors including dissolved oxygen, turbidity and pH with two groups being identified, that is, metals that increased with increasing salinity and metals that increased with increasing turbidity. In sediment, metal concentrations showed little seasonal variation. There were, however, significant spatial differences in metal concentrations, with muddy, high organic areas of the estuary consistently having highest concentrations of metals as compared to other sites. These results suggest a high degree of heavy metal contamination in the Mhlathuze Estuary and also stress the importance of incorporating sediment metal analysis in any assessment of metal pollution in estuarine environments.

Key words: Estuaries, heavy metals, pollution.

INTRODUCTION

Rapid industrial and urban development has previously been linked to high concentrations of heavy metals recorded in the Richards Bay Harbour (Vermeulen and Wepener 1999). The Mhlathuze Estuary is located adjacent to Richards Bay harbour. The estuary and the harbour originally formed a single system called the Richards Bay estuary, but during the development of the deep water port, the original estuary was divided into half by a berm wall (Begg, 1978). The new mouth was

created for the Mhlathuze Estuary on the southern side of the harbour. This area was reserved for environmental protection and declared a marine protected area (Begg, 1978).

Industrial activity in the Mhlathuze catchment includes manufacturing of metal products by some industries, while many others use metals in processing their products. The Mhlathuze estuarine system has a potential to be polluted by heavy metals from effluents

*Corresponding author. E-mail: MzimelaH@unizulu.ac.za. Tel: +27 (35) 902 6737. Fax: +27(35) 902 6750.

discharged by these industries. Wepener and Vermeulen (1999) reported the estuary as having a low freshwater input in winter and floods occur during summer in the Richards Bay area. These floods initiate in the upper reaches and the freshwater may flush heavy metals into the estuary from the upper reaches.

The adjacent harbour is periodically dredged and the dredger spoil is either discharged on the beach or a few kilometres offshore. In both instances, there is a possibility of the dredger spoil finding its way into the estuary (Cyrus and Wepener, 1998).

The possibility of spoil ingressions was predicted by the CSIR (1993) and observed by Begg (1978) who reported the ingressions of the fine sediment from the dredger spoil south towards the mouth of the estuary during visual environmental audits. Cyrus and Wepener (1998) also reported the ingressions of the fine sediment into the mouth of the estuary. A dramatic increase in the percentage of mud (<63 μm) was observed around the estuary in the area south of the Mhlathuze estuary (CSIR, 1993; Cyrus and Wepener, 1998). The mud fraction is known to be the component of sediment on to which most of the metals will adhere (Newman and Watling, 2007). This ingressions brought about physical change and was reported as having impacted on certain components of the biota (CSIR, 1993).

Metals occur in aquatic environments either as dissolved ions or as metals bound to particular matter. The dissolved fraction is usually the bioavailable fraction however it is toxic to biota in estuarine environments (Silva et al., 2006). The particulate fraction is adsorbed to organic matter, organic fluvic and humic acids (Krupadam et al., 2006). A high amount of heavy metals may be locked onto sediments. These are metals that have been scavenged from the water column on to the particulate matter and later onto proximal sediments (Sarkar et al., 2004). In shallow estuaries such as the Mhlathuze Estuary, metals have a potential to be resuspended and thus become bio-available (Wepener and Vermeulen, 2005). They may also be available to benthic and bottom feeding organisms during feeding (Shirneshan et al., 2012). As the normal estuarine function rely on the mixing of both sea water and freshwater from the river, the type of metal species present in the particular system is determined by the chemistry of that freshwater/sea interface.

There is very little information available concerning the environmental and physicochemical processes that regulate the existence of metals in South African estuarine systems. Generally, in estuarine and marine environment, the behavior of heavy metals is governed by a number of physicochemical and environmental factors such as salinity, valence state and association with organic radicals, dissolved oxygen and pH (Cox and Micaela, 2005). These processes can remove metals dissolved in water by adsorption of metals onto particulate matter or cause resuspension of metals from

sediment (Sarkar et al., 2004). Any physicochemical change that reduces the hydrophylic complexation of dissolved trace metals enhances the bioavailability of that metal by increasing the concentration of the free metal ions (Krupadam et al., 2006); thereby causing the bioavailable metal becomes toxic to biota. Since physical and chemical factors such as pH and salinity are dynamic in estuaries, metals behave differently across estuarine environments. Mhlathuze estuary is a marine dominated estuary with salinity normally ranging from 20-35 ppt.

In view of possible harbour expansion and the introduction of a metal mining plant in the catchment, the objectives of this study were to determine baseline information on the bioaccumulation of metals in water and sediment of the Mhlathuze Estuary.

MATERIALS AND METHODS

Quarterly water and sediment samples were collected in the Mhlathuze Estuary from April 1996 to December 1997. Samples were collected from the sampling sites (Figure 1).

Water samples

The surface water variables were determined *in situ* at each site using a Surveyor 3 Hydrolab connected to an H₂O water quality multiprobe: pH, water temperature, dissolved oxygen and percentage oxygen saturation, turbidity, and salinity. Water samples collected at each site were analysed by the analytical laboratory of Mhlathuze Water Scientific Services for orthophosphates, sulphates and fluorides. Two surface water samples were collected at each site, one was filtered through a 0.45 μm cellulose acetate filter and the other unfiltered.

The unfiltered sample represents total metal concentrations whereas the filtered sample represents dissolved metal concentrations. The samples were frozen until analysed for metal concentration in the laboratory. The samples were thawed and pre-concentration was carried out by acidifying 250 ml water with 10 ml of 55% nitric acid and 5 ml perchloric acid in Erlenmeyer flasks and evaporating to 5 ml on a hotplate (Standard Methods, 1998). Samples were made up to 50 ml with double distilled water.

Metal analyses

Aluminium, Cr, Cu, Fe, Mn and Zn in water and sediment were measured by flame furnace atomic absorption spectrophotometry using a Varian SpectrAA 50B spectrophotometer fitted with a deuterium arc background corrector. Calibration was carried out using matrix matched calibration standards. Analytical accuracy was determined using Standard Reference Material (SRM) of the National Bureau of Standards: standard for trace elements in water (SEM 1643c) and Buffalo River sediment (SRM 2704). Recoveries were within 10% of the certified values.

Statistical analyses

Statistical analyses of the data were performed using Tukey ANOVA multiple comparison test to measure ad hoc significant differences. Significance was regarded at the $P < 0.05$ significance level. Baseline normalization was performed using Fe as a normalizing metal [metal ($\mu\text{g/g}$)/Fe ($\mu\text{g/g}$)]. The principal component analysis (PCA) was used to determine the relationships between

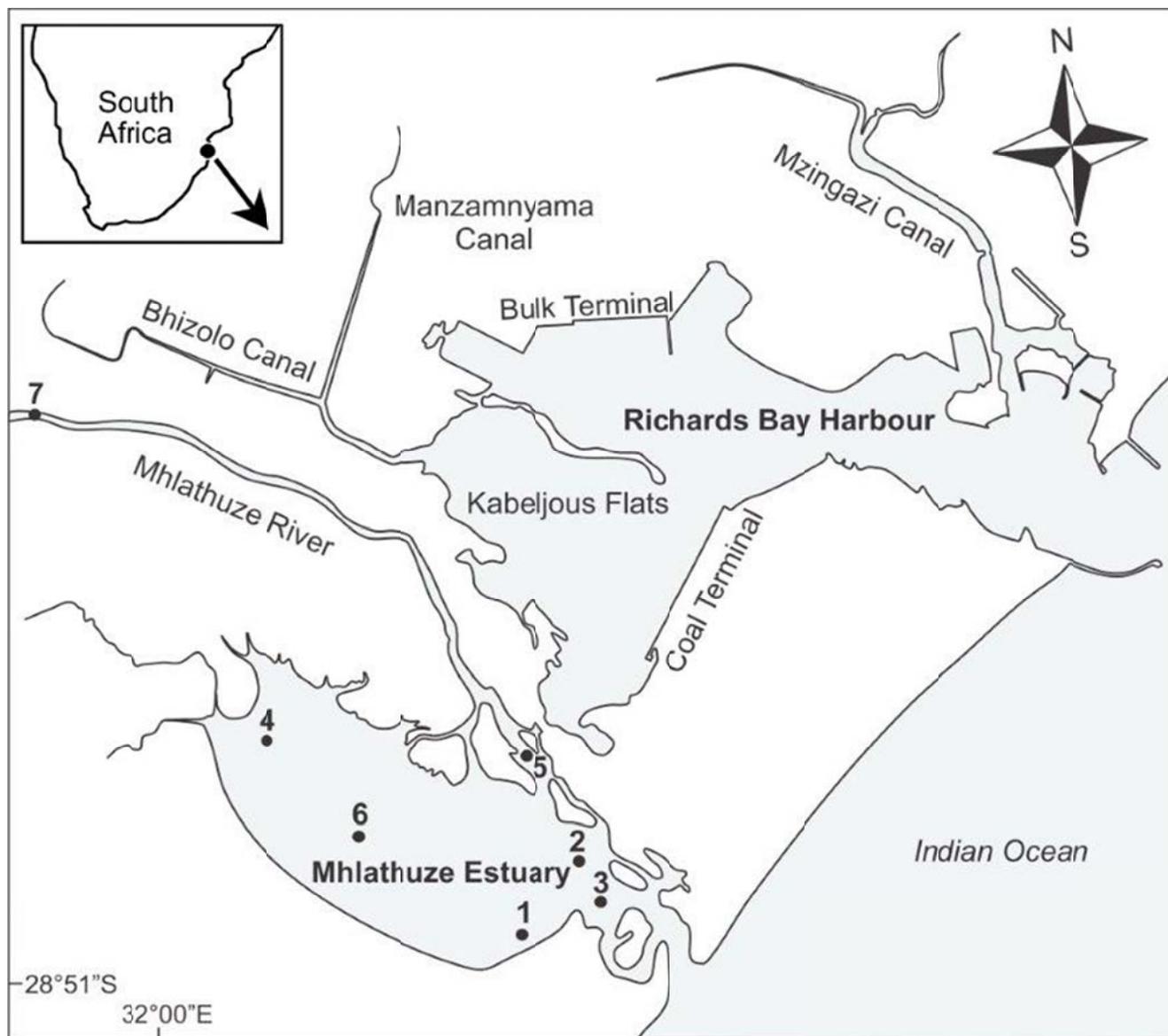


Figure 1. Map of Richards Bay Harbour and Mhlathuze Estuary showing sampling sites.

metals in water, sediment and environmental variables.

RESULTS AND DISCUSSION

Changes in the selected physico-chemical variables of the Mhlathuze Estuary are summarized in Table 1. Temperatures remained fairly constant at all sites during the quarterly surveys reflecting the natural seasonal temperature fluctuations in a subtropical environment. Only the water temperatures at site 4 seemed consistently different from those measured at the other sampling sites during the particular survey. Turbidity varied seasonally with elevated turbidities during Spring and Summer. Turbidities were elevated at site 4 when

compared with the historical data. This could be attributed to the deposition of sediments from the catchment into the estuary. The deposition resulted in the buildup of very fine sediments on the bottom of the estuary. Due to its shallow nature, the strong tidal prism and strong prevailing north-easterly or south westerly winds, the soft bottom sediments can be brought into resuspension, with potential ensuing deleterious effects to the aquatic biota. Although resuspension is a natural process, the spoil from dredging in the harbour has been shown to exacerbate the situation.

Recently, it was shown that ingression of fine sediments into the estuary from the marine environment was causing a build-up of very fine sediments in the

Table 1. Quarterly physico-chemical values recorded at five sites in the Mhlathuze Estuary for the sampling period from April 1996 to December 1997. Historical data in the original estuary before the construction of the harbour are represented by A after the construction of the harbour are presented by B.

Season	Site	Temp (°C)	Turbidity(NTU)	O ₂ (mg/l)	O ₂ (%)	Salinity (‰)	pH	PO ₄ (mg/l)	NO ₃ (mg/l)	SO ₄ (mg/l)
Historical data A ¹		21.00	6.00	7.58	101.00	28.00	8.10	0.02	0.00	NA
Historical data B ²		NA	NA	NA	NA	32.8	NA	0.017	0.067	NA
Autumn 1996	1	21.00	3.7	7.07	98.5	36.5	7.87	0.23	ND	2583
Autumn 1996	2	20.09	4.6	6.91	96.9	36.5	7.92	0.09	ND	2667
Autumn 1996	3	22.95	DL	6.84	94.3	36.7	7.79	0.24	ND	2639
Autumn 1996	4	19.91	31.7	6.34	88.2	29.2	7.72	0.16	ND	2222
Autumn 1996	5	19.86	BDL	8.00	89.4	0.8	7.91	0.25	0.80	107
Winter 1997	1	19.09	5.0	8.53	119.5	34.0	4.19	BDL	ND	2600
Winter 1997	2	20.15	19.6	7.42	98.8	30.4	5.40	BDL	ND	3100
Winter 1997	3	17.36	4.4	7.82	108.2	34.5	8.78	BDL	ND	3000
Winter 1997	4	16.31	6.0	7.41	96.8	30.5	7.56	BDL	ND	2600
Winter 1997	5	21.45	6.5	8.31	88.6	8.1	7.49	BDL	ND	410
Spring 1996	1	21.03	6.0	7.63	108.2	34.4	7.82	0.18	ND	3860
Spring 1996	2	20.96	26.0	7.66	109.5	34.4	7.86	0.12	ND	3700
Spring 1996	3	21.88	24.0	7.74	110.3	34.4	7.88	BDL	ND	3140
Spring 1996	4	24.12	5.0	7.48	107.2	34.2	7.78	BDL	ND	3860
Spring 1996	5	25.47	14.0	8.01	108.1	22.2	7.67	BDL	ND	2420
Summer 1996	1	23.62	8.0	7.74	115.3	34.6	8.58	0.10	ND	3300
Summer 1996	2	24.00	5.0	7.88	115.2	34.9	8.44	0.17	ND	2700
Summer 1996	3	25.84	4.0	8.23	12.2	34.9	8.49	0.17	ND	3150
Summer 1996	4	30.41	15.0	7.57	114.8	34.0	8.52	0.20	ND	2850
Summer 1996	5	24.58	28.0	7.94	114.7	14.2	8.44	ND	ND	ND
Autumn 1997	1	22.10	16.0	6.94	101.4	32.3	8.45	BDL	ND	4000
Autumn 1997	2	24.05	12.0	6.80	90.9	32.9	8.40	0.21	ND	3500
Autumn 1997	3	23.80	18.0	7.46	108.1	32.5	8.52	0.09	ND	2900
Autumn 1997	4	23.20	14.0	6.42	88.2	24.2	8.32	0.19	ND	2200
Autumn 1997	5	19.51	26.0	7.50	86.6	0.3	8.25	0.45	0.50	32
Winter 1997	1	19.18	15.0	5.84	105.6	34.2	8.40	0.21	0.07	2881
Winter 1997	2	19.16	22.0	8.01	105.7	35.1	8.40	0.21	0.07	2959
Winter 1997	3	19.04	20.0	8.12	105.1	35.1	8.40	0.20	0.06	3026
Winter 1997	4	14.76	24.0	8.22	94.8	6.5	7.74	0.18	0.06	189
Winter 1997	5	20.22	46.0	9.11	91.2	0.4	7.27	0.11	0.49	24
Spring 1997	1	21.15	14.0	7.62	103.8	35.0	8.82	0.17	BDL	2928
Spring 1997	2	20.03	28.0	7.45	98.4	36.5	8.64	0.13	0.14	1806
Spring 1997	3	18.71	17.5	20.30	102.0	35.3	8.80	0.22	0.12	3137
Spring 1997	4	21.72	10.0	7.03	89.8	29.4	8.36	0.13	0.11	2285
Spring 1997	5	21.42	29.0	21.42	78.4	0.3	8.68	0.06	0.21	32
Summer 1997	1	22.67	20.0	7.16	84.2	4.1	7.70	0.08	0.28	370
Summer 1997	2	22.66	25.0	6.58	76.1	0.2	7.43	0.06	0.46	185
Summer 1997	3	21.76	17.0	7.37	86.5	5.5	7.66	0.10	0.36	477
Summer 1997	4	22.48	45.5	7.36	85.4	0.7	7.78	BDL	0.35	46
Summer 1997	5	22.16	10.00	5.10	59.70	0.20	7.19	0.07	0.28	12

BDL = Below detection limit. ND = No data. ¹Hemens *et al.* (1971) and ²Hemens *et al.* (1976).

mouth of the estuary and embayment (Cyrus and Wepener, 1998). This ingress was attributed to

dredging activities in Richards Bay Harbour. Salinity remained constant throughout the system during the

study with the exception of summer 1997 where the salinity at all sites was below 6‰. The reduced salinity during summer 1997 was a result of the flood that occurred during the sampling trip.

Salinity measured at site 5 was consistently lower than other sites during a particular survey. Dissolved oxygen was also constant throughout the estuary. Site 3 which was the site located at the mouth of the estuary had consistently elevated dissolved oxygen concentrations.

This was also the case for sulphate and fluoride. Concentrations at site 5 were consistently different from those measured at any of the other sampling sites during the particular survey.

During summer 1997, sulphate concentrations were lower as compared to those measured in other seasons. Nutrients (nitrates and orthophosphates) showed little variations during the study (Table 1).

During the construction of the harbour, nutrients level increased due to redistribution of anaerobic silt dredge from several meters below the surface.

Hemens et al. (1976) speculated that this was due to the bottom consisting of redeposited silt that had been depleted of its soluble nitrogen, or that the release of nitrogen from dead and decaying plankton had decreased, together with plankton densities, due to the opening of the new mouth.

The present study showed substantially higher nutrient levels than during the 1970s. It is unlikely that runoff from the catchment could contribute to the high nitrate concentrations measured at Sites 5 and 4, since low nutrient levels were recorded in the lower reaches of the river and at Site 1 (Table 1).

According to Wepener and Vermeulen (1999), the source of the nutrients is possibly related to fixation of nitrogen by blue-green algae in the muds of the vast mangrove areas.

Another potential source of nutrients they mentioned was sewage runoff from the surrounding rural settlements was indicated by high faecal coliform counts the authors obtained (Wepener and Vermeulen, 1999). Seasonal and spatial organic content (mean \pm standard error) of sediment samples from the Mhlathuze Estuary are presented in Table 2.

Mean organic content were highest during summer 1996 and lowest during autumn 1996. The highest mean organic content was recorded at Site 4 with the lowest levels measured at site 3.

Metals in water

Temporal and spatial variations of metals in water

Metals in the water column generally did not show any significant differences between seasons with the exception of December 1997 where concentrations were significantly different from the rest of the seasons. During

Spring 1997, Cu and Pb concentrations were also significantly higher.

The increase in metals during summer 1997 was probably related to resorption of metals bound to suspended particles during river flood conditions that prevailed during the sampling trip. A general trend of a reduction in metals was observed during autumn 1997. This reduction was attributed to dilution of waterborne metals by freshwater due to floods. According to Krupadam (2006) wide variations in water-borne metal concentration within estuaries are normally related to the degree of fresh water contribution or the presence of industrial effluents.

Total metal concentrations in water samples showed little spatial variation (Table 2). Only Pb concentrations significantly differed between Site 3 at the mouth and Site 5 which is located up the Mhlathuze River. This is probably related to the short residence time of water in the estuary.

About 90% of water from the estuary is being drained during each tidal cycle (Begg, 1978). The residence time of water may be too short to allow for major spatial variations of metals in water. The highest Pb concentrations in water recorded at Site 3 suggests the mouth as the source of lead pollution into the estuary. Lead may have been discharged with the fine sediments during dredger spoil on the breach, which were transported into the estuary through the mouth.

The elevated concentrations of Fe, Al, Zn and Cr recorded in the water from the Mhlathuze Estuary are in agreement with the results reported by Vermeulen and Wepener (1999, 2005) for metals in water from the adjacent Richards Bay Harbour (Table 4). When compared with historical concentrations reported from the original Richards Bay Estuary, only Zn concentrations were higher during the present study. Hemens et al. (1976) commented on the high Zn concentrations recorded at that time as "reason for concern". Their study was, however, conducted before the completion of the harbour.

The high metal concentrations measured in this study could therefore be related to subsequent activities in the catchment and adjacent harbour area. Wave borne metals could also enter the estuary from the harbour via tidal gates. These tidal gates that are no longer in use were built to serve as a connection between the water in the harbour and the estuary. During high tide water can be observed overtopping over the tidal gates (personal observation) and it is therefore highly likely that metals originating in the harbour will find its way into the estuary. The concentrations of metals from this study were slightly elevated when compared with metal concentrations in the water of other estuaries on the east coast of South Africa (Table 4). It must be borne in mind that surveys by Hemens et al. (1970, 1976) were undertaken between 20 and 30 years ago and that these concentrations may have increased in the intervening

Table 2. Comparisons of dissolved metal concentrations in water (A) and metals in sediment (B) in the Mhlathuze Estuary with corresponding metal concentrations in other estuaries on the eastern seaboard of South Africa and in other countries.

Estuary	Al ($\mu\text{g/l}$)	Cr ($\mu\text{g/l}$)	Cu Fe ($\mu\text{g/l}$)	Fe ($\mu\text{g/l}$)	Mn ($\mu\text{g/l}$)	Pb ($\mu\text{g/l}$)	Zn ($\mu\text{g/l}$)	Reference
Water								
Mhlathuze	990.0	48.0	39.1	907.0	48.2	130.15	66.5	This study
Kynsna	-	0.1	0.2	81	5	0.6	0.3	a
Gamtoos	-	-	0.6	372	41	0.6	1.1	c
Swartkops	-	-	3.9	275	41	1.5	3.6	d
Sundays	-	1.3	3.2	334	18	0.7	2.4	e
Bushmans	-	0.4	1.8	302	10.2	0.2	0.5	f
Kosi Bay	-	-	1.1	-	-	1.0	5.7	i
St Lucia E	-	-	3.3	68.8	-	39.2	2.3	j
St Lucia E	-	-	17	2000	-	-	11.7	i
Richards Bay	-	-	1.7	-	-	1.9	-	k
Richards Bay	-	-	4.0	-	-	4.2	3.8	i
Richards Bay	504.4	23.6	50.8	782.4	80.7	-	85.4	l
Durban	-	-	27	800	-	117	287	i
East London	-	-	42.4	183.0	16.3	23.9	27.6	Fatoki
Port Elizabeth	-	-	11.3	21.9	4.2	16.8	16.2	Fatoki
Sunderban	-	-	-	175.0	-	0.20	9.7	GandK
Sediment								
Mhlathuze	18677.4	64.4	12.2	20606.9	13.5	45.6	45.6	This study
Kynsna	-	21	5	-	14	17	17	a
Gamtoos	-	15	5	9180	7	16	16	c
Swartkops	-	5	18	20800	31	55	55	d
Sundays	-	38	16	72	18	57	57	e
Bushmans	-	22	3	7330	5	13	13	f
Kosi Bay	-	150	61	60000	19	72	72	i
St Lucia E	-	7	2	3000	0.8	3.4	3.4	i
St Lucia E	-	-	9.9	23640	24	98	98	k
Richards Bay	-	74.8	24.04	5814	17.47	87.16	87.16	j
Richards Bay	-	110.3	19.22	31762.7	-	95.54	95.54	l
Richards Bay	31323.4	388	57	40000	117	287	287	i
Durban	-	-	183.0	18114.0	549.0	332.0	332.0	m
East London	-	-	82.3	15182.0	499.0	126	126	m
Port Elizabeth	-	-	-	10068	25.15	3448.4	3448.4	n
Sunderban	-	-	-	16600	29	54	54	o
Victoria	-	16.0	9.0	-	-	-	-	-

References: a, Watling and Watling, 1982a; c, Watling and Watling, 1982c; d, Watling and Watling, 1982d; e, Watling et al., 1982; f, Watling and Watling, 1983b; g, Watling et al., 1985, 1985; i, Cloete et al., 1979; j, Oliff et al., 1986; k, Connell *et al.*, 1975; l, Vermeulen and Wepener, 1999; m., Fatoki and Mathabatha 2001; n. Guhathakurta and Kariva 2000, Tanner et al., 2000.

period.

Metals such as Zn and Cr are important constituents of industrial mining and domestic effluents (Khan et al., 2005). High concentrations of these metals may be a direct consequence of anthropogenic contamination from these activities. It is not possible to comment on the high Al levels since there is no historical data (Hemens et al., 1976) to compare with it. However, it is highly likely that the current levels are due to a combination of

anthropogenic sources (the nearby aluminium smelter complexes, dredging of sediments in Richards Bay Harbour and natural leaching and weathering processes in the catchment).

Metals in sediment

Metals concentrations in the sediment were in elevated

orders of magnitude above the concentrations recorded in water. According to Soumady and Asokan (2011), sediments represent the most concentrated pool of metals in aquatic environments, metals that can be assimilated by aquatic organisms resident in those sediments. Since those organisms form a primary food source for bottom feeding fish, the accumulation of metals by such fish potentially depends on uptake from food as well as from water (Shulkin et al., 2003; Silva et al., 2006). Various bioaccumulation studies also found concentrations of metals in the estuarine environments which were in orders of magnitude higher in sediments than in water (Allen, 1993; Lim et al., 2012).

No significant temporal differences were recorded for metals in the sediment. This may be due to most metals being present in sediment as precipitates or in an undissolved state.

In estuarine systems, these metals are not bio-available except to organisms that are resident in sediment (Williams et al., 1998). Metals would be taken up and absorbed through the skin, or be ingested with food particles in benthic feeders.

Highest metal concentrations in the sediment were recorded for Fe, Al and Zn (Table 4). These metals also displayed the highest accumulation in the particulate matter in the water column. Watling and Watling (1982a-d) also reported high concentrations of Fe and Zn from sediments in Gamtoos, Swartkops, and Sunday River estuaries (Table 4), although concentrations in these estuaries were lower than those in this study.

There were significant spatial variations in metals concentrations (Table 3). With the exception of Al and Pb, most metals differed significantly between Sites 3 and 4. Metals concentrations were highest at Site 4, and with the exception of Cu, all metals had lowest concentrations at Site 3. The reasons could be attributed to the differences in substrate types and the amount of organic material.

Site 4 is in the middle of the embayment and contains mainly fine sediment. It is also the site with the highest organic content when compared with the rest of the sites. Site 3 is at the mouth of the estuary and is dominated by coarse sand. It is also the lowest in terms of organic content (Table 3).

The metals in the Mhlathuze Estuary probably exist as particulate matter or precipitated metals. Their presence in sediment may be predominantly due to a result of anthropogenic activities and ingression with fine dredged spoil from the harbour (Van den Hurk et al., 1997).

The metals are then precipitated onto and into the sediments. According to Sarkar et al., 2004 and Magesh et al. (2011), high loads of heavy metals are normally concentrated in the fine sediments. It is likely that most of the particulate bound metals entered the estuary during the ingression of into the Mhlathuze Estuary which took place when dredger spoil was deposited on the beach north of the estuary (Wepener and Cyrus, 1997; Mackay

and Cyrus, 1999). Wave action and the near-shore current would have resulted in contaminated fine silt drifting into the estuary. The very high levels of Al in sediment may either be from geological leaching, as the area is known for its high Al metal content (Kwazulu Natal Business, 2013), or from pollution effects such as dredger spoil (Wepener and Cyrus, 1997).

Concentrations of Cu and Pb in sediment were low, ranging from 20-50 $\mu\text{g/g}$. These metals exist mostly as dissolved ions in the water column hence their low concentrations in sediment.

Copper is also known to form complexes with organic matter (Sarkar et al., 2004). The highest Cu concentrations in the sediment (at site 4) could be attributed to the complexation of Cu with organic ligands since the highest organic content was also recorded at this site (Table 4). The presence of high organic content in estuaries can decrease toxicity of metals such as copper by binding copper to organic ligands (DePalmer et al., 2011).

Chromium concentrations were elevated in sediments of the Mhlathuze Estuary (Table 4). High concentrations of Cr may be a result of contamination from the harbour due to sediment bound metals entering the estuary as discussed in the previous paragraphs. The results suggest equal amounts of Cr being exchanged between dissolved fractions in pore water and particulate fractions in sediment. This is because the percentage of particulate and dissolved Cr reported in this study were almost equal and also both the fractions were significantly different between seasons. Studies in estuarine areas show that dissolved and particulate Cr are present in almost equal quantities with the flocculation processes increasing Cr^{3+} concentrations in the salinity that are below normal sea water (Zwolsman and van Eck, 1999).

Results of this study show that metals vary spatially and temporally in water at the Mhlathuze estuary. Although there are minor variations of metals in sediment these results, the concentrations are higher than those recorded in other estuaries along in the eastern seaboard (Table 2). Seasonal variation in the Mhlathuze Estuary may be as a result of the metal loads that may be delivered by the river or sea. Spatial differences may be as a result of behaviour of metals in response to gradients in the chemistry of the water body and the nature of the sediment.

The important factor that results in variation of metals between sites closer to the mouth in the Mhlathuze Estuary is the residence time of water in the estuary. The tidal cycle in the estuary affects the sites next to the mouth (Site 1, 2 and 3). Water from these sites is almost completely replaced during a tidal cycle. The quality of water brought in during each tidal cycle would be similar resulting in more or less similar values for sites next to the mouth (sites 1, 2 and 3). Salinity values from these sites are also similar and was close to sea water. Sites 4

Table 3. Spatial heavy metal concentrations (means \pm standard error) in water (total dissolved and particulate) (μgL^{-1}) and sediment ($\mu\text{g.g}^{-1}$) in the Mhlathuze Estuary. All references to significant differences are made in the text and are not indicated in the table.

Parameter	Turbidity	Salinity	Organic	Dissolved O ₂	pH	Total	Suspended	Dissolved
Aluminium								
Turbidity	1							
Salinity	-0.64*	1						
Organic	0.02	-0.27	1					
Dissolved O ₂	0.06	0.11	0.10	1				
pH	-0.18	0.45*	-0.04	0.22*	1			
Total	0.23	-0.24*	-0.19	-0.11	-0.58*	1		
Suspended	-0.28*	0.36*	-0.21*	-0.37*	-0.15	0.117	1	
Dissolved	0.05	0.03	-0.32*	0.13	-0.22*	0.44*	0.35*	1.00
Chromium								
Turbidity	1.00							
Salinity	-0.70*	1.00						
Organic	-0.02	-0.16	1.00					
Dissolved O ₂	0.01	0.10	-0.04	1.00				
pH	-0.19*	0.40*	-0.01	0.11	1.00			
Total	-0.02	0.08	-0.28*	-0.17	0.19	1.00		
Suspended	0.24*	-0.29*	0.01	-0.34	0.33*	0.66*	1.00	
Dissolved	0.25	-0.05	-0.29*	-0.02	-0.23*	0.51*	0.26*	1.00
Copper								
Turbidity	1.00							
Salinity	-0.53*	1.00						
Organic	-0.10	-0.26*	1.00					
Dissolved O ₂	-0.07	0.12	-0.05	1.00				
pH	-0.10	0.34*	-0.06	0.28*	1.00			
Total	-0.20*	0.44*	0.17	0.14	0.55*	1.00		
Suspended	-0.07	0.12	-0.46*	-0.16	-0.27*	-0.12	1.00	
Dissolved	0.07	0.30*	-0.06	-0.09	-0.11	0.29*	0.11	1.00
Manganese								
Turbidity	1.00							
Salinity	-0.61*	1.00						
Organic	-0.06	-0.26*	1.00					
Dissolved O ₂	0.01	0.17	-0.10	1.00				
pH	-0.19*	0.46*	-0.09	0.19	1.00			
Total	0.11	0.03	-0.41*	-0.06	0.01	1.00		
Suspended	0.48*	-0.51*	0.17	-0.36*	-0.10	0.13	1.00	
Dissolved	0.11	0.03	-0.23*	-0.09	-0.03	.52*	-0.13	1.00
Iron								
Turbidity	1.00							
Salinity	-0.52*	1.00						
Organic	-0.22*	-0.22	1.00					
Dissolved O ₂	-0.04	0.22*	-0.20*	1.00				
pH	-0.11	0.43*	-0.04	0.27*	1.00			
Total	0.11	0.09	-0.30*	0.08	-0.50*	1.00		
Suspended	0.62*	0.42	-0.23*	-0.13	-0.43*	0.508*	1.00	
Dissolved	-0.07	0.20*	-0.52*	-0.12	0.08	0.36*	0.05	1.00

Table 3. Contd.

Parameter	Turbidity	Salinity	Organic	Dissolved O ₂	pH	Total	Suspended	Dissolved
Lead								
Turbidity	1.00							
Salinity	-0.60*	1.00						
Organic	-0.05	0-.27*	1.00					
Dissolved O ₂	0.06	0.18*	-0.13	1.00				
pH	-0.18*	0.44*	-0.02	0.16	1.00			
Total	-0.20*	0.44*	0.05	0.13	0.58*	1.00		
Suspended	-0.11	0.14	0.07	-0.28*	0.27*	-0.00	1.00	
Dissolved	-0.16	0.35*	-0.18*	0.19	-0.06	0.41*	-0.63*	1.00
Zinc								
Turbidity	1.00							
Salinity	-0.62*	1.00						
Organic	0.03	-0.29*	1.00					
Dissolved O ₂	0.06	0.13	-0.12	1.00				
pH	-0.20*	0.43*	-0.02	0.24*	1.00			
Total	0.01	0.10	-0.22*	0.32*	-0.11	1.00		
Suspended	0.20*	-0.34*	0.08	-0.39*	-0.04	0.21*	1.00	
Dissolved	0.12	0.01	0.04	-0.23*	0.12	0.16	0.15	1.00

and 5 however were different. Site 4 is in the basin and site 5 up the river. There is limited tidal influence on these sites and consequently they have different levels of metals in comparison to the former sites. The low levels of metals consistently reported in water and sediment up river at site 5, when compared with the other sites lead to the conclusion that the ingress of sediment from the harbour as the source of most of the high metal concentrations found in sediments of the Mhlathuze Estuary. Harbour sediments have been reported by various authors as highly polluted environments, and a possible source of metal contamination in surrounding water bodies e.g. Victoria Harbour, (Tanner et al., 2000) East London and Port Elizabeth (Fatoki and Mathabatha, 2001), Tolo Harbour (Owen and Sandhu, 2000), Richards Bay Harbour (Vermeulen and Wepener, 2005) and Klaipeda Harbour (Galkus et al., 2012).

Temporal variations of metals in sediment could not be observed in the Mhlathuze Estuary. This is because of the relative stability of metals in sediments as well as variation of metals concentrations at different sites. Metals varied spatial because of the different substrates found in the Mhlathuze Estuary and their variability in accumulation of metals. According to Cox and Micaela (2005), heavy metal distribution in estuarine and marine deposits is influenced by sediment texture, clay content, organic carbon, iron hydrous oxides and carbonates. These components differ in the manner in which they adsorb metals (Newman and Watling, 2007). The clay-rich sediment and organic carbon rich sediment tend to contain higher metal content as compared to sand

dominated regions. Mud has a very fine texture and it usually accumulates most of the metals. According to Herut and Sandler (2006), clay minerals readily absorb heavy metal and consequently clay-rich sediments tend to contain higher contamination levels than sand-dominated deposits. Fine sediments contribute by having large specific areas with many attachment sites for metals. Organic coating also occurs easily in fine sediments (Mortimer and Rae, 2000). Types of substrate sediments in the Mhlathuze Estuary are described in Cyrus and Wepener (1998). Sites 1, 2 and 4 have high mud and organic content (Table 3). They also had high metals concentration when compared with sandy sites such as sites 3 and 5, which had low concentrations of heavy metals in the sediment (Table 4).

One method used to determine the level of contamination of metals in sediment is the simple ratio between the concentration of a metal and the concentration of the normaliser. The conditions that are considered in selecting a normalizer is that the metal should be abundant, naturally occurring and should not be influenced by anthropogenic sources. Because of these conditions, metals that are considered as suitable for the normalization of metals in sediment are Al and Fe (Newman and Watling, 2007). For this study, Fe was considered more suitable due to the presence of aluminium smelters located around the harbour area with a possibility of estuarine sediment contamination from the smelters' effluents. An attempt to normalize the sediment metals using Al showed results with very low R² values, a high number of data points that behaved as

Table 4. Mean seasonal heavy metal concentrations in water (total, dissolved and particulate) ($\mu\text{g}\cdot\text{g}^{-1}$) in the Mhlathuze Estuary. All references to significant differences are made in the text and are not indicated in the table.

Sample	Site 1	Site 2	Site 3	Site 4	Site 5
Organic content	5.12 \pm 1.18	4.55 \pm 1.05	2.51 \pm 0.76	11.17 \pm 1.73	4.53 \pm 1.73
Aluminium					
Total	1995.8 \pm 1554.2	42705 \pm 3159.8	2060.0 \pm 1554.3	5814.2 \pm 4973.1	2630.0 \pm 2029.6
Dissolved	632.8 \pm 281.9	721.0 \pm 403.6	990.3 \pm 580.4	1546.5 \pm 1090.4	939.3 \pm 522.0
Particulate	513.5 \pm 347.9	564.3 \pm 356.6	537.3 \pm 234.2	837.0 \pm 408.0	332.8 \pm 143.5
Sediment	22044.9 \pm 7119.2	21202.1 \pm 6081.8	10303.3 \pm 3514.6	29118.4 \pm 7631.0	17230.9 \pm 4012.4
Chromium					
Total	37.5 \pm 13.0	61.8 \pm 26.7	32.8 \pm 13.8	47.0 \pm 27.3	26.3 \pm 16.2
Dissolved	46.0 \pm 10.7	65.3 \pm 10.8	46.3 \pm 12.1	48.8 \pm 17.7	33.5 \pm 15.1
Particulate	44.8 \pm 14.3	51.0 \pm 15.2	50.5 \pm 16.8	53.8 \pm 20.6	40.0 \pm 16.5
Sediment	84.1 \pm 15.1	42.4 \pm 12.2	41.7 \pm 8.9	107.9 \pm 16.5	55.6 \pm 10.8
Copper					
Total	53.1 \pm 10.2	51.3 \pm 7.2	48.3 \pm 6.6	38.3 \pm 9.0	21.8 \pm 6.0
Dissolved	42.0 \pm 13.4	52.3 \pm 16.2	50.8 \pm 15.9	38.3 \pm 15.9	14.5 \pm 4.4
Particulate	2.3 \pm 1.2	19.0 \pm 11.2	9.3 \pm 11.2	9.3 \pm 5.9	5.2 \pm 3.0
Sediment	12.1 \pm 1.8	8.4 \pm 2.5	8.8 \pm 2.3	22.72.0	11.7 \pm 2.7
Iron					
Total	1732.5 \pm 1054.9	3900.8 \pm 2817.1	1872.5 \pm 1241.4	4119.5 \pm 3286.1	2585.0 \pm 2077.8
Dissolved	655.0 \pm 218.8	787.1 \pm 292.4	961.8 \pm 584.7	1317.5 \pm 864.6	730.0 \pm 406.7
Particulate	1542.5 \pm 869.0	5598.3 \pm 4224.3	2067.5 \pm 954.3	1142.5 \pm 315.4	1797.5 \pm 857.7
Sediment	23132.3 \pm 2303.6	18715.9 \pm 4456.7	12585.8 \pm 33473	31280.7 \pm 3428.7	21048.5 \pm 5641.2
Manganese					
Total	77.8 \pm 11.7	110.5 \pm 24.7	69.8 \pm 12.0	109.0 \pm 46.9	82.8 \pm 20.2
Dissolved	42.8 \pm 8.2	88.0 \pm 39.6	45.8 \pm 9.1	40.0 \pm 6.4	61.3 \pm 20.2
Particulate	36.8 \pm 8.5	60.8 \pm 13.0	43.8 \pm 14.9	121.7 \pm 58.74	70.5 \pm 18.8
Sediment	274.2 \pm 44.2	308.2 \pm 89.4	165.3 \pm 38.7	731.5 \pm 141.2	335.5 \pm 66.6
Lead					
Total	168.8 \pm 22.9	233.5 \pm 37.8	240.0 \pm 41.5	193.0 \pm 55.0	78.8 \pm 19.7
Dissolved	167.5 \pm 72.2	129.5 \pm 35.8	186.0 \pm 62.8	130.3 \pm 65.8	37.5 \pm 12.5
Particulate	59.0 \pm 27.76	57.8 \pm 23.47	67.0 \pm 35.6	62.5 \pm 25.97	39.5 \pm 19.5
Sediment	18.0 \pm 3.8	14.1 \pm 3.5	9.1 \pm 2.1	18.7 \pm 4.2	12.3 \pm 2.8
Zinc					
Total	66.8 \pm 3.8	76.2 \pm 6.4	63.0 \pm 4.3	119.5 \pm 59.1	43.8 \pm 5.2
Dissolved	68.8 \pm 8.3	83.5 \pm 13.1	74.5 \pm 6.5	64.5 \pm 18.7	59.8 \pm 7.3
Particulate	41.8 \pm 10.4	69.0 \pm 14.3	47.0 \pm 12.5	114.2 \pm 59.8	47.0 \pm 9.9
Sediment	54.7 \pm 4.6	35.0 \pm 9.0	33.1 \pm 7.1	74.1 \pm 4.7	37.7 \pm 7.0

outliers and metals Cr, and Zn were not significantly different ($P < 0.05$). Normalization plots of metals using Fe are presented in Figure 2. The ratios of metals to Fe were calculated and linear regressions were represented for metals Al, Cr, Mn, Pb and Zn. The R^2 values recorded are displayed in the graph. The regression recorded was significantly different for all metals. The outliers observed in the regression graphs for metals Al, Cr and Cu

indicated increased concentrations of metals due to anthropogenic influence. Regression of Al and Fe was the lowest as compared to other metals suggesting an increase of Al from background concentrations. In the comparison of metals and physicochemical parameters using principal component analysis, the two axes retained 60.8% of the variances from the sample data. The multivariate PCA analysis, based on metals in water,

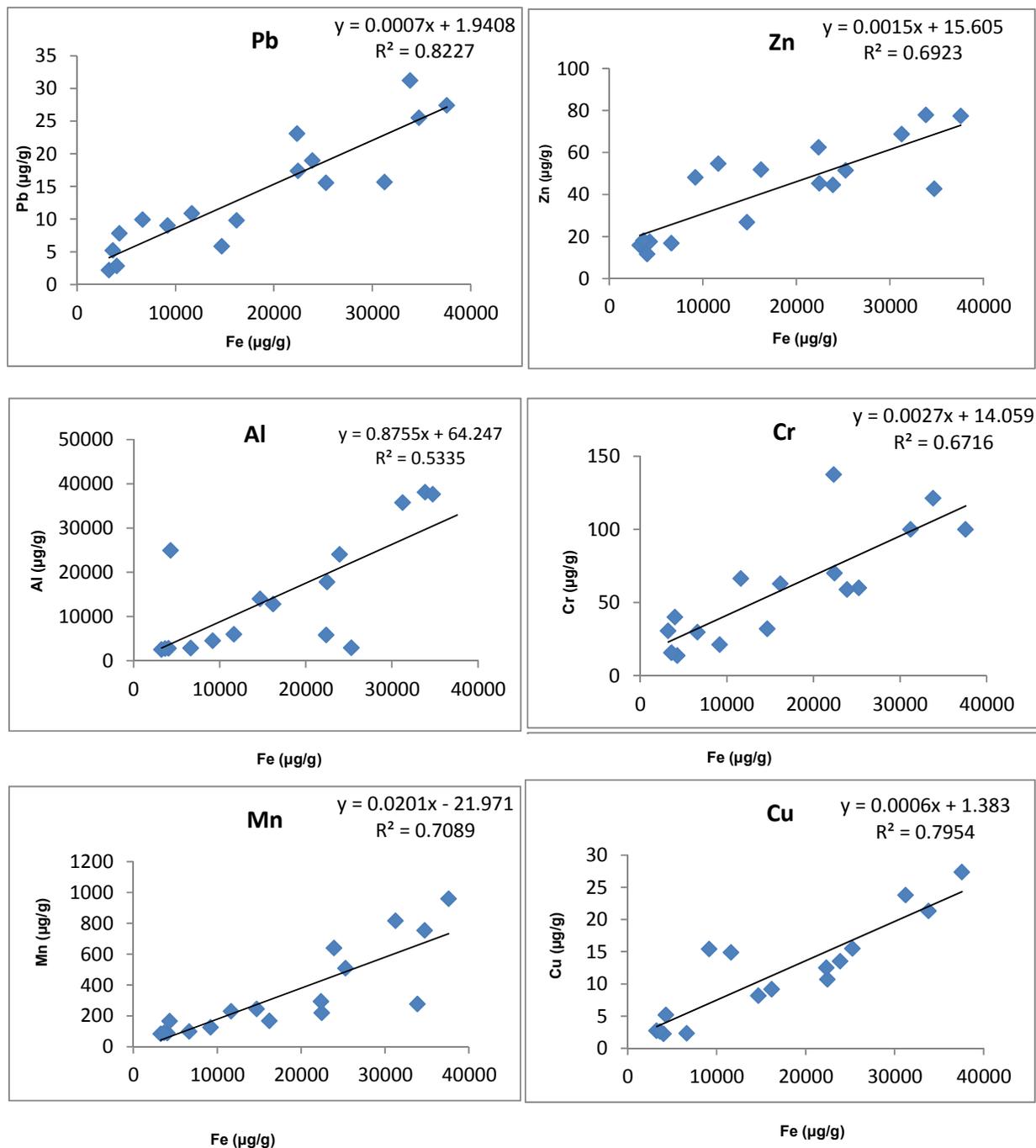


Figure 2. Normalised linear regression plots of Al, Cr, Mn, Pb and Zn concentrations ($\mu\text{g/g}$) to Fe ($\mu\text{g/g}$).

sediment and physicochemical data is plotted in Figure 3. The data for metals from the different phases and the physicochemical parameters influencing them formed three distinct groups. A fourth group consisted of nutrients and water quality parameters.

The first group consisted of sediment metals and the organic content. The correlation of metals in sediment suggested the increase of metals in sediment with an

increase in the sediment organic content. Sediment metals in the estuary increased and were found in high concentration in the areas such as the basin at Site 4 that had high organic matter. The mouth area, however, had less organic content and low concentrations of metals.

The particulate concentrations of Al, Pb Cu and Zn formed the second group that increased with an increase in dissolved oxygen, pH and temperature. These

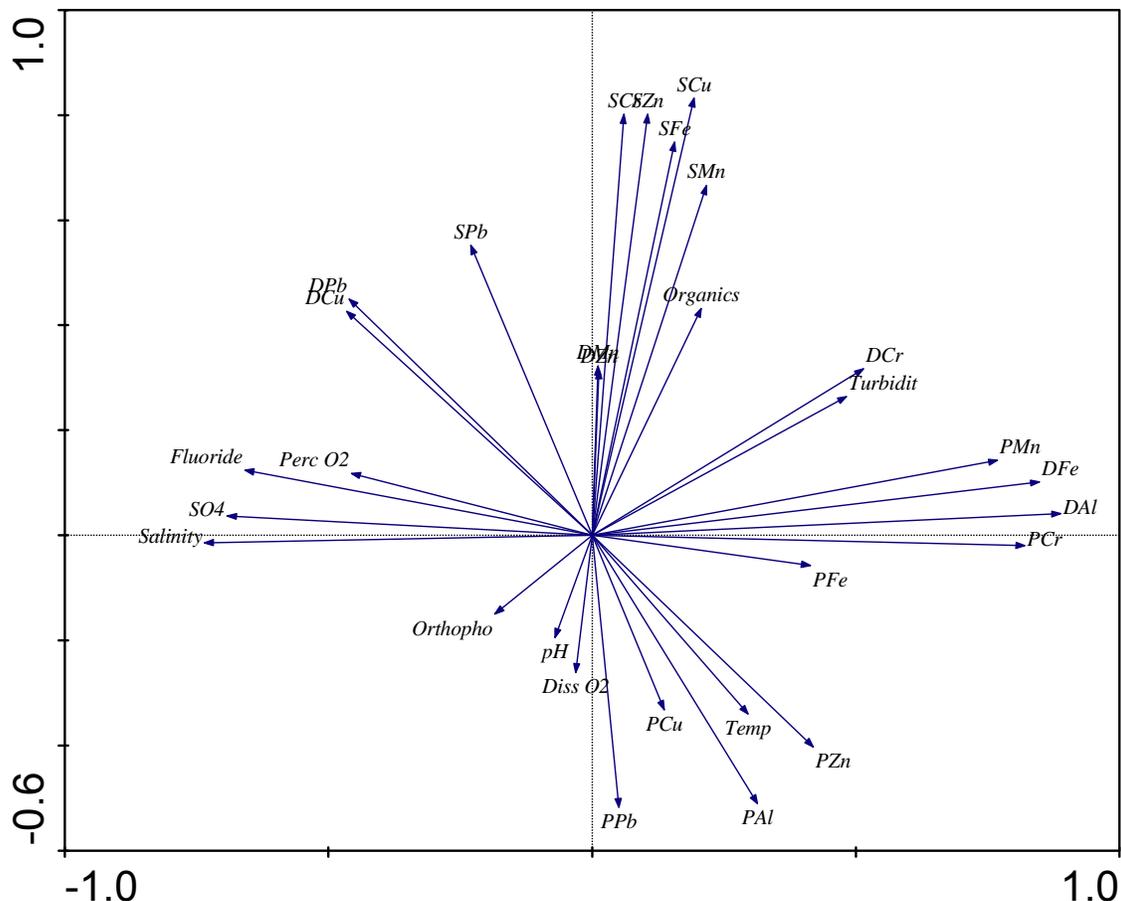


Figure 3. Principal component analysis biplots of particulate (P), dissolved (D) and sediment (S) concentrations (60.8% of variance explained)

conditions were found in the shallow waters towards the mouth of the estuary. This suggests that precipitation is the important process for the increased of these metals in the particulate phase. In the third group, the dissolved concentrations of Al, Cr and Fe and the particulate concentrations of Cr, Mn and Fe were correlated with turbidity, suggesting increasing concentrations of these metals in the basin where turbidity was high due to re-suspension as a result of the shallow nature of the estuary and the very fine bottom sediment. Dissolved Zn and Mn concentrations were both influenced by different factors to the other dissolved metal concentrations. This was also observed in the behaviour of dissolved Mn and Zn in other estuaries on the KZN eastern seaboard (unpublished data) where dissolved concentrations of both Mn and Zn increased in areas of high salinity and high turbidity. The correlations of dissolved Cu and Pb concentrations were probably related to the very low dissolved concentrations of these metals recorded in the Mhlathuze Estuary. The increase in salinity and percentage oxygen at the mouth of the estuary coincided with increases in sulphates and fluoride concentrations as identified by the water quality group. This suggests the

sea as the source of the fluorides and sulphates in the estuary as these chemicals are observed in very low concentrations in the upstream sites.

Heavy metals discharged directly from industrial effluents, as well as those diffusing from activities in the harbour and from runoff storm water; result in contamination of water and harbour sediments (Vermeulen and Wepener, 1999). Material that was dredged from the harbour was deposited on to the beach north of the estuary mouth. The dredge spoil is then taken up by wind and currents to the estuary mouth thereby transferring metal contamination into the estuary. The harbour authority has been looking at various ways of disposing of the spoil as an environmental exercise to mitigate the potential pollution of the estuary. The method that was recommended by CRUZ (Wepener and Cyrus, 1997; Cyrus and Wepener, 1998) of disposal a few kilometres offshore is environmentally sustainable. This would result in the pollution from the spoil becoming more diffuse and not drifting towards the Mhlathuze Estuary.

The value of an estuary for resource harvest, habitat for fish and other invertebrates and for aesthetic beauty can never be overestimated (Breen and McKenzie, 2001).

The idea of keeping the southern side of the original Richards Bay Estuary for resource protection proved to be a good environmental exercise. It was to ensure perpetuation of biodiversity and resource protection. It is however being affected by activity in surrounding areas. This is shown by the findings of this study in terms of metal pollution in the Mhlathuze Estuary.

Further studies are needed to clearly point to the actual sources of pollutants in the Mhlathuze Estuary. Activities such as mining on the boundary waters (Armah et al., 2010), and periodic dredging of the harbour have been found to have a marked effect on the accumulation of metals in estuarine environments (Van der Hurk et al., 1997; Galkus et al., 2012). A high concentration of these metals has an effect on biota of estuaries. This could be made worse by a number of factors. Plans are underway to expand the Port of Richards Bay. The operation of EXARRO Sands, a heavy metal company that has recently built on the catchment of the Mhlathuze River, has been in operation for about 10 years. Both these and other future developments may impact negatively on the estuary in terms of metal pollution.

Conflict of Interests

The author(s) have not declared any conflict of interests.

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